

PURE TITANIUM BUILDING MATERIAL AND
METHOD OF MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a pure titanium building material resistant to secular discoloration for constructing external walls of buildings, and reinforcing members, and a method of manufacturing such a pure titanium material.

Description of the Related Art

A titanium material has a surface coated with an oxide film, which is perfectly resistant to rusting, is excellent in corrosion resistance and has desirable mechanical properties. Titanium building materials have been watched with keen interest for their excellent properties.

Recent development of the waterfront and the recent progressively deteriorating environmental conditions around buildings due to acid rain brought about various problems. Recent, severe environmental conditions to which titanium building materials are exposed discolor the titanium building materials from silver white into brownish color by aging. Since the discolored titanium materials do not glitter in beautiful metallic colors any longer and spoil the aesthetic design of buildings. Although it is possible to renew the original beautiful appearance of titanium materials discolored by aging by maintenance work including wiping or polishing, such maintenance work is very expensive, and some parts of

buildings reject maintenance work. Accordingly, studies have been made to develop titanium materials resistant to secular discoloration.

A titanium or a titanium alloy material disclosed in JP-A 10-8234 has a surface finished in a surface roughness $R_a = 3 \mu\text{m}$ or below and coated with an oxide film of 20 \AA or above in thickness to suppress secular discoloration. Titanium and titanium alloy materials disclosed in Jpn. Pat. No. 3255610 have an oxide film of 100 \AA or below and a surface layer having a specified C content.

A technique intended to solve problems resulting from secular discoloration by specifying the C content of a surface layer is disclosed also in JP-A 2001-348634. A titanium sheet manufacturing process according to this technique anneals a cold-rolled titanium sheet at 750 to 800°C for 3 to 5 min to make a layer having a high C content, which is considered to cause secular discoloration, vanish.

Requirements for suppressing the secular discoloration of titanium building materials have progressively become severe in recent years, and the development of titanium materials further resistant to secular discoloration has been earnestly desired. Test data mentioned in the foregoing three reference documents are qualitative and not quantitative. Titanium materials must be evaluated by a more precise evaluation system to develop titanium materials meeting the recent severe requirements.

Although various pure titanium building materials re-

sistant to secular discoloration have been placed on the market, pure titanium building materials having further improved secular-discoloration resistance are demanded because the severity of design of buildings have been progressively increasing and maintenance cost has been progressively increasing in recent years.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a pure titanium material more resistant to secular discoloration than conventional titanium materials.

Inventors of the present invention studied various titanium materials to solve the foregoing problems, and repeated sever evaluation of secular-discoloration resistance of the titanium materials and found that specific impurities contained in the titanium materials dominate the secular-discoloration resistance of the titanium materials.

Pure titanium and titanium alloys are used for forming pure titanium building materials. Most pure titanium building materials are formed of industrial pure titanium of Grade 1 JIS containing impurities in a small quantity and excellent in formability. Even if titanium building materials are formed of a material not containing titanium scraps and containing only industrial titanium Grade 1, JIS, i.e., sponge titanium, the titanium building materials inevitably contain various impurities in small contents. Chemical requirements for industrial titanium Grade 1, JIS specify impurity contents

including oxygen content and iron content in terms of formability. Any attention has not been paid to such impurity contents at all in improving secular-discoloration resistance.

The inventors of the present invention found that pure building materials formed of pure titanium having specific impurity contents below predetermined levels are scarcely subject to secular discoloration and have made the present invention.

According to the present invention, a pure titanium building material is formed of pure titanium having an Fe content of 0.08% by mass or below, a Nb content of 0.02% by mass or below, and a Co content of 0.02% by mass or below.

Preferably, the pure titanium building material has a surface oxide film of 170 Å or below in thickness. Although a pure titanium building material having a thicker surface oxide film has lower secular-discoloration resistance, the pure titanium building material has a beautiful silver white color, and the growth of the surface oxide film can be effectively suppressed when the pure titanium building material has the composition defined as above and the surface oxide film is 170 Å or below. Therefore, the pure titanium building material having a surface oxide film of 170 Å or below in thickness is not subject to secular discoloration to an extent that spoils aesthetic design and maintains silver white appearance.

A pure titanium building material manufacturing method

according to the present invention includes the steps of: forming a pure titanium building material of pure titanium having an Fe content of 0.08% by mass or below, a Nb content of 0.02% by mass or below and a Co content of 0.02% by mass or below, pickling the pure titanium building material; and heating the pickled pure titanium building material at a temperature X (°C) in the range of 130 to 280°C for a heating time T (min) so as to meet a condition expressed by: $T \geq 239408 \times X^{-2.3237}$.

The heating step forms a surface oxide film of a proper thickness effective in suppressing detrimental coloring and reduces impurities that cause discoloration as well. Thus, the pure titanium building material manufactured by the pure titanium building material manufacturing method is highly resistant to secular discoloration.

Having very high secular-discoloration resistance far higher than that of conventional titanium or titanium alloy building materials, the pure titanium building material of the present invention is very useful as a building material for constructing buildings to which high aesthetic design is essential, those exposed to sea wind and acid rain, those requiring high maintenance cost and those difficult to maintain. Thus, the pure titanium building material of the present invention is very industrially useful.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects, features and advantages of

the present invention will become more apparent from the following description taken in connection with the accompanying drawings, in which:

Fig. 1 is a graph of assistance in explaining an AES method of measuring the thickness of an oxide film; and

Fig. 2 is a graph showing the relation between heating time and heating temperature effective in improving secular-discoloration resistance.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It is the most characteristic feature of a pure titanium building material according to the present invention that the secular discoloration of the pure titanium building material develops very slowly even when the pure titanium building material is used for constructing a building exposed to a severe environment.

Although titanium or titanium alloy building materials resistant to secular discoloration are available on the market, their secular-discoloration resistance is insufficient. Even a conventional corrosion-resistant pure titanium building material discolors with time. The inventors of the present invention found that specific impurities contained in the titanium material of the pure titanium building material develops the secular discoloration of the pure titanium building material and that a pure titanium building material formed of a pure titanium containing impurities in controlled impurity contents are highly resistant to secular

discoloration even under severe environmental conditions, and have made the present invention.

A pure titanium building material in a preferred embodiment according to the present invention is formed of pure titanium having an Fe content of 0.08% by mass or below, a Nb content of 0.02% by mass or below, and a Co content of 0.02% by mass or below. Fe, Nb and Co contained in a pure titanium forming a pure titanium building material cause the development of secular discoloration of the pure titanium building material. This fact was discovered by the inventors. The development of the secular discoloration of the pure titanium building material can be remarkably retarded by controlling the Fe, Nb and Co contents of the pure titanium below the foregoing specified Fe, Nb and Co contents. In specifying an impurity content, "X% by mass or below" signifies that pure titanium does not contain the impurity at all or contains the impurity in an ignorable amount. The content is expressed in "percent by mass", which will be simply expressed by "percent" hereinafter. Preferably, Fe content is 0.06% or below (more preferably, 0.05% or below), Nb content is 0.015% or below (more preferably, 0.01% or below) and Co content is 0.015% or below (more preferably, 0.01% or below).

To obtain pure titanium having Fe, Nb and Co contents not exceeding the foregoing specified Fe, Nb and Co contents, the Fe, Nb and Co contents of a raw titanium material are adjusted. More concretely, the impurity contents of sponge titanium, i.e., a raw titanium material, are measured, and use

the sponge titanium if the sponge titanium has Fe, Nb and Co contents not exceeding the foregoing specified Fe, Nb and Co contents.

The term "pure titanium" used herein signifies a substance containing Fe, Nb and Co in contents not exceeding the specified Fe, Nb and Co contents, inevitable impurities, and Ti as the remainder.

Preferably, the thickness of the surface oxide film of the pure titanium building material as manufactured is 170 Å or below. The pure titanium building material having the surface oxide film of 170 Å or below in thickness and having a composition specified by the present invention has a beautiful silver white color characteristic of titanium. The pure titanium building material of the present invention effectively suppresses the growth of the surface oxide film that causes discoloration and hence the pure titanium building material has is excellent as a building material.

The thickness of the surface oxide film can be adjusted by adjusting conditions for growing a surface oxide film during the manufacture of the pure titanium building material. The surface oxide film grows when the pure titanium building material is exposed to oxygen contained in the atmosphere during an annealing process and is removed by pickling. Therefore, the thickness of the surface oxide film can be adjusted by adjusting vacuum for vacuum annealing, the temperature of the workpiece at the start of exposure of the vacuum annealed workpiece to the atmosphere or the degree of rinsing

after a pickling process. More concretely, the thickness of a sample surface oxide film and conditions for forming a surface oxide film are adjusted repeatedly to determined desirable conditions.

Although there are not any particular restrictions on a method of measuring the thickness of the surface oxide film, the thickness can be measured by, for example, Auger electron spectroscopy. As shown in Fig. 1, the thickness of the surface oxide film can be determined by multiplying sputtering time required for oxygen concentration to decrease to a middle oxygen concentration between a maximum oxygen concentration and a base oxygen concentration by sputtering rate, i.e.,
$$(\text{Thickness of surface oxide film}) = (\text{Sputtering time } t) \times (\text{Sputtering rate}).$$
The sputtering rate may be estimated from a sputtering rate at which a SiO_2 film is deposited by sputtering conforming to measuring sputtering conditions.

Generally, a pure titanium building material manufacturing method of the present invention includes, at least an ingot manufacturing process, a hot-rolling process, a cold-rolling process and a finishing process. Conditions for those processes may be the same as those for generally known processes. The finishing process subsequent to the cold-rolling process must be carefully designed because the finishing process has significant influence on the surface property of the titanium material.

For example, the finishing process for finishing the titanium material is a vacuum annealing process (VA process)

or an atmospheric annealing and pickling process (AP finishing process). It is understood that the surface oxide film of a titanium material finished by the VA process contains a large amount of C which causes secular discoloration. Therefore a pickling process is preferably employed in finishing the titanium material. The pure titanium building material manufacturing method may include an additional process, provided that the additional process does not spoil the effect of pickling. For example, a workpiece processed by pickling may be finished by light rolling (skin pass) using dulling rolls in a dull surface to improve the design (sharpness) of the workpiece.

When the surface of the workpiece is treated by pickling in the finishing process, a titanium material having high secular discoloration resistance can be obtained by subjecting the pickled workpiece to a heat treatment process that heats the pickled workpiece at a temperature X ($^{\circ}\text{C}$) in the range of 130 to 280 $^{\circ}\text{C}$ for a heating time T (min) so as to meet a condition expressed by: $T \geq 239408 \times X^{-2.3237}$. Heating the workpiece at temperatures in the range of 130 to 280 $^{\circ}\text{C}$ does not cause detrimental discoloration that spoils the design, and the heat treatment process meeting the condition expressed by the expression has further improved secular discoloration resistance. Although the reason why the heat treatment process improves the secular discoloration resistance is not clearly known, it is considered that the heat treatment process changes the construction of the oxide film.

Sometimes, detrimental discoloration occurs when the workpiece is heated at a high temperature not lower than 250°C (250 to 280°C) for a long time in the atmosphere. Therefore it is desirable to heat the workpiece for a heating time not longer than 30 min, more preferably 10 min or below, when the workpiece is to be heated at such a high temperature. Even if discoloration occurs, the workpiece is colored at the initial stage of discoloration in a very light golden color, which improves the design instead of spoiling the same. In some cases, the heating may be stopped at such an initial stage to provide a pure titanium building material discolored in a very light golden color.

The heat treatment process heats the workpiece in either a vacuum atmosphere or an atmospheric atmosphere. Any upper limit heating time is specified for the heat treatment process that heats the workpiece in a vacuum atmosphere because there is no possibility that the workpiece is discolored when the workpiece is heated in a vacuum atmosphere.

The pure titanium building material of the present invention thus fabricated has very high secular discoloration resistance as compared with conventional titanium or titanium alloy building materials.

Examples of the present invention will be described.

Example 1

Specimens

Specimens Nos. 1 to 21 of high-purity titanium (5N, Purity: 99.999% or higher) containing impurity elements in

predetermined impurity element contents and respectively having different chemical compositions were produced to examine the effect of impurity contents on secular discoloration.

Titanium raw materials respectively having chemical compositions shown in Table 1 were melted in a vacuum button melting furnace and ingots of a weight in the range of 100 to 200 g were produced. The ingots were heated by a first heating process at 1000°C for 1 hr, and then the ingots were hot-rolled by a first hot-rolling process to obtain 6 mm thick plates. The 6 mm thick plates were heated by a second heating process at 1000°C for 10 min and by a third heating process at 850°C for 1 hr, and the thus heated 6 mm thick plates were hot-rolled by a second hot-rolling process to obtain 3 mm thick sheets. The thus hot-rolled sheets were annealed by an annealing process at 800°C for 10 min, and the annealed 3 mm thick sheets were air-cooled. Oxide scale formed on one surface of each of the annealed 3 mm thick sheets was removed by surface grinding in a depth of 0.5 mm. Then, the 3 mm thick sheets were cold-rolled by a cold-rolling process to obtain about 1 mm thick pure titanium sheets. The about 1 mm thick pure titanium sheets were subjected to a final finishing process that annealed the about 1 mm thick pure titanium sheets under the following annealing conditions.

Temperature: 650°C

Time for heating up to 650°C: 5 hr

Soaking time: 3 hr

Vacuum: 10^{-6} torr

Cooling: Exposed to the atmosphere at 200°C or below.

Test (Secular Discoloration Resistance Test)

The effect to Fe, Nb and Co as impurities on secular discoloration was tested by immersing the pure titanium sheets in the specimens Nos. 1 to 21 in a sulfuric acid solution of pH4 heated at 60°C for three days to simulate a situation where building materials are exposed to acid rain and sea wind, the specimens Nos. 1 to 21 were rinsed to remove the sulfuric acid solution remaining on the specimens Nos. 1 to 21 completely so that the sulfuric acid solution may not promote discoloration, and then the specimens Nos. 1 to 21 were dried. Then, the color difference (ΔE^*) of the specimens were measured using color-difference meter.

In determining color difference, a three-dimensional color space is assumed, the color of the specimen is decomposed into three axial components, i.e., a component on one lightness axis (white/black), and two hue axes (red/green and yellow/blue), and the color is represented by three-dimensional coordinates. Color difference is the difference in color between the specimens represented by the distance between points specified by the coordinates representing the colors. A smaller color difference corresponds to smaller degree of discoloration. When ΔE^* is less than 5, it is judged that secular discoloration is sufficiently suppressed. Measured data is shown in Table 1, in which underlined values are those outside ranges specified by the present invention.

As obvious from Table 1, the specimens Nos. 13 to 15 having Fe contents outside the Fe content range specified by the present invention are conspicuously discolored, i.e., color differences are large. Similarly, the specimens Nos. 16 and 17 having Nb contents and Co contents outside a Nb content range and a Co content range specified by the present invention, the specimen Nos. 19 and 21 having Nb contents outside the specified Nb content range, and the specimens Nos. 18 and 20 having Co contents outside the specified Co content range are discolored excessively and have color differences ΔE^* exceeding 5, even though those specimens have Fe contents within the specified Fe content range.

On the other hand the specimens Nos. 1 to 12 having Fe, Nb and Co contents within the specified Fe, Nb and Co content ranges have color differences ΔE^* below 5, and high secular discoloration resistance.

Example 2

Specimens

Pure titanium sheets of about 1 mm in thickness in specimens Nos. 22 to 45 having chemical compositions shown in Table 2 were produced by the same process as that by which the specimens Nos. 1 to 21 in Example 1 were produced.

The specimens Nos. 22 and 23 were subjected to pickling instead of vacuum annealing in the last process; that is, the specimens Nos. 22 and 23 were treated by atmospheric annealing at 700°C for 20 s after cold rolling, salt immersion at 550°C for 15 s, and pickling of 40 μ m in thickness using a mixture

heated at 40°C and containing 15% by mass nitric acid and 1.5% by mass hydrofluoric acid.

Test

The thickness of the surface oxide film of each of the specimens was measured before immersing the specimens in a sulfuric acid solution for a secular discoloration resistance test. More concretely, the specimens were subjected to ultrasonic cleaning in acetone, the specimens were dried and oxygen concentration was measured under the following conditions.

Apparatus: Scanning Auger Spectroscope, PH1650 (Parkin Elmer Co.)

Primary electrons: Energy 5 keV, Current: 300 nA,
Incident angle: 30° to the normal to the specimen

Analyzed area: about 10 μm \times about 10 μm

Ion sputtering: Energy: 3 keV, Current: 25 mA, Incident angle: about 58° to the normal to the specimen, Sputtering rate about 1.9 nm/min (SiO_2 equivalent)

The thickness of the surface oxide film was calculated using measured data. The thickness was determined by multiplying sputtering time (measured time) required for oxygen concentration to decrease to a middle oxygen concentration between a maximum oxygen concentration and a base oxygen concentration by sputtering rate of about 1.9 nm/min.

The color differences ΔE^* of the specimens were measured similarly after the measurement of the thickness of the surface

oxide film. Measured data is shown in Table 2.

As obvious from Table 2, the pure titanium materials having Fe, Nb and Co contents within the specified Fe, Nb and Co content ranges have color differences ΔE^* below 5 and have high secular discoloration resistance.

The color differences ΔE^* of the specimens finished by vacuum annealing are greater than those of the specimens finished by pickling. Thus, it is preferable to finish pure titanium building materials by pickling.

It was found that the specimens having the surface oxide films of a thickness not greater than 170 Å have desirably small color differences ΔE^* and sufficient secular discoloration resistance.

Example 3

Specimens

Pure titanium sheets in specimens Nos. 46 to 83 were produced by using a pickling process similar to that employed in Example 2. The specimens Nos. 46 to 83 had an Fe content of 0.06 or 0.03% by mass, an Nb content of 0.001% by mass and a Co content of 0.001% by mass. The specimens were finished by heat treatment processes under conditions shown in Table 3. Values of $239408 \times X^{-2.3237}$ were calculated.

Test

The color differences of the specimens Nos. 46 to 83 were measured similarly to those of the specimens in Example 1. Measured data is shown in Table 4.

The measured data shown in Table 4 proves that finishing

pure titanium building materials by a finishing process including pickling and subsequent heating treatment improves the secular discoloration resistance remarkably.

Heating times for the heat treatment processes P, Q and R were shorter than the minimum heating time expressed by $239408 \times X^{-2.3237}$ and hence the effect of the heat treatment processes P, Q and R is somewhat low. Thus, it was known that the heating time T must meet an expression: $T \geq 239408 \times X^{-2.3237}$ for the further improvement of the secular discoloration resistance. Fig. 2 shows the relation between heating time and heating temperature.

Although the specimen processed by the heat treatment process S has a small color difference ΔE^* , the specimen was colored in a golden color due to heating in the atmosphere at a high temperature of 280°C for a long time of 150 min. Although pure titanium building materials colored in such a golden color are unsuitable when noncolored pure titanium building materials are desired, pure titanium building materials colored in such a golden color have uses.

Although the color difference ΔE^* of the specimen processed by the heat treatment process L specifying a heating temperature of 280°C and a heating time of 120 min is greater than that of the specimen processed by the heat treatment process S, the color difference ΔE^* is satisfactorily small. The specimen processed by the heat treatment process L was colored less than that processed by the heat treatment process S, and was colored in a golden color.

Heating time must be 30 min or shorter, more preferably, 10 min or shorter to prevent coloring due to high-temperature heating in the atmosphere.

Table 1

Specimen No.	Fe content (% by mass)	Nb content (% by mass)	Co content (% by mass)	ΔE^*
1	0.08	0.02	0.02	4.5
2	0.08	0.01	0.01	4.0
3	0.08	0.005	0.005	3.3
4	0.08	0.001	0.001	2.9
5	0.06	0.02	0.02	2.5
6	0.06	0.01	0.01	2.4
7	0.06	0.005	0.005	2.1
8	0.06	0.001	0.001	1.9
9	0.03	0.02	0.02	2.2
10	0.03	0.01	0.01	2.1
11	0.03	0.005	0.005	1.8
12	0.03	0.001	0.001	1.3
13	<u>0.10</u>	0.001	0.001	9.1
14	<u>0.15</u>	0.001	0.001	14.7
15	<u>0.20</u>	0.001	0.001	18.2
16	0.08	<u>0.03</u>	<u>0.03</u>	8.9
17	0.03	<u>0.03</u>	<u>0.03</u>	6.9
18	0.08	0.005	<u>0.03</u>	6.6
19	0.08	<u>0.03</u>	0.005	6.3
20	0.03	0.005	<u>0.03</u>	5.4
21	0.03	<u>0.03</u>	0.005	5.7

Table 2

Specimen No.	Fe content (% by mass)	Nb content (% by mass)	Co content (% by mass)	Finishing process	Thickness of oxide film (Å)	ΔE^*
22	0.08	0.02	0.02	Pickling	140	2.8
23	0.08	0.01	0.01	Pickling	120	1.6
24	0.08	0.005	0.005	Pickling	110	1.2
25	0.08	0.001	0.001	Pickling	120	0.8
26	0.06	0.02	0.02	Pickling	100	2.1
27	0.06	0.01	0.01	Pickling	130	1.3
28	0.06	0.005	0.005	Pickling	160	1.0
29	0.06	0.001	0.001	Pickling	150	0.7
30	0.03	0.02	0.02	Pickling	160	1.8
31	0.03	0.01	0.01	Pickling	170	1.1
32	0.03	0.005	0.005	Pickling	170	0.8
33	0.03	0.001	0.001	Pickling	110	0.6
34	0.08	0.02	0.02	Vacuum annealing	130	4.5
35	0.08	0.01	0.01	Vacuum annealing	140	4.0
36	0.08	0.005	0.005	Vacuum annealing	130	3.3
37	0.08	0.001	0.001	Vacuum annealing	150	2.9
38	0.06	0.02	0.02	Vacuum annealing	150	2.5
39	0.06	0.01	0.01	Vacuum annealing	160	2.4
40	0.06	0.005	0.005	Vacuum annealing	170	2.1
41	0.06	0.001	0.001	Vacuum annealing	110	1.9
42	0.03	0.02	0.02	Vacuum annealing	90	2.2

43	0.03	0.01	0.01	Vacuum annealing	80	2.1
44	0.03	0.005	0.005	Vacuum annealing	160	1.8
45	0.03	0.001	0.001	Vacuum annealing	120	1.3

Table 3

Heating process	Heating conditions			$239408 \times X^{2.3237}$
	Heating temperature (°C)	Soaking time (min)		
(A)	130	3	Atmospheric	2.93
(B)	130	20	Atmospheric	2.93
(C)	130	60	Atmospheric	2.93
(D)	130	120	Atmospheric	2.93
(E)	200	1.1	Atmospheric	1.08
(F)	200	20	Atmospheric	1.08
(G)	200	60	Atmospheric	1.08
(H)	200	120	Atmospheric	1.08
(I)	280	0.5	Atmospheric	0.49
(J)	280	20	Atmospheric	0.49
(K)	280	60	Atmospheric	0.49
(L)	280	120	Atmospheric	0.49
(M)	130	120	Vacuum	2.93
(N)	200	120	Vacuum	1.08
(O)	280	120	Vacuum	0.49
(P)	130	2	Atmospheric	2.93
(Q)	200	0.5	Atmospheric	1.08
(R)	280	0.2	Atmospheric	0.49
(S)	280	150	Atmospheric	0.49

Table 4

Specimen No.	Fe content (% by mass)	Nb content (% by mass)	Co content (% by mass)	Finishing process	Heat treatment process	ΔE^*
46	0.06	0.001	0.001	Pickling	(A)	0.4
47	0.06	0.001	0.001	Pickling	(B)	0.4
48	0.06	0.001	0.001	Pickling	(C)	0.3
49	0.06	0.001	0.001	Pickling	(D)	0.3
50	0.06	0.001	0.001	Pickling	(E)	0.4
51	0.06	0.001	0.001	Pickling	(F)	0.3
52	0.06	0.001	0.001	Pickling	(G)	0.3
53	0.06	0.001	0.001	Pickling	(H)	0.2
54	0.06	0.001	0.001	Pickling	(I)	0.3
55	0.06	0.001	0.001	Pickling	(J)	0.3
56	0.06	0.001	0.001	Pickling	(K)	0.2
57	0.06	0.001	0.001	Pickling	(L)	0.2
58	0.06	0.001	0.001	Pickling	(M)	0.4
59	0.06	0.001	0.001	Pickling	(N)	0.3
60	0.06	0.001	0.001	Pickling	(O)	0.3
61	0.03	0.001	0.001	Pickling	(A)	0.3
62	0.03	0.001	0.001	Pickling	(B)	0.2
63	0.03	0.001	0.001	Pickling	(C)	0.2
64	0.03	0.001	0.001	Pickling	(D)	0.2
65	0.03	0.001	0.001	Pickling	(E)	0.2
66	0.03	0.001	0.001	Pickling	(F)	0.2
67	0.03	0.001	0.001	Pickling	(G)	0.2
68	0.03	0.001	0.001	Pickling	(H)	0.1
69	0.03	0.001	0.001	Pickling	(I)	0.2
70	0.03	0.001	0.001	Pickling	(J)	0.1
71	0.03	0.001	0.001	Pickling	(K)	0.1

72	0.03	0.001	0.001	Pickling	(L)	0.1
73	0.03	0.001	0.001	Pickling	(M)	0.2
74	0.03	0.001	0.001	Pickling	(N)	0.2
75	0.03	0.001	0.001	Pickling	(O)	0.2
76	0.06	0.001	0.001	Pickling	(P)	0.7
77	0.06	0.001	0.001	Pickling	(Q)	0.7
78	0.06	0.001	0.001	Pickling	(R)	0.7
79	0.06	0.001	0.001	Pickling	(S)	0.1
80	0.03	0.001	0.001	Pickling	(P)	0.6
81	0.03	0.001	0.001	Pickling	(Q)	0.6
82	0.03	0.001	0.001	Pickling	(R)	0.6
83	0.03	0.001	0.001	Pickling	(S)	0